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MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

Dedicated to the memory of L. A. Nud'ga, a leading scientist in the field of Russian chitinology

Synthesis in a Gel and Sorption Properties of N-2-Sulfoethyl Chitosan

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Abstract—A new procedure was developed for preparation of chelate amino-containing polymer N-2-sulfoethyl chitosan by synthesis in a gel through the reaction between chitosan and sodium 2-bromoethanesulfonate, yielding a polymer with the degree of substitution of up to 0.5. The structure of the resulting polymers was confirmed by ^{1}H NMR spectroscopy. The sorption characteristics with respect to transition and alkaline-earth metal ions were determined for the cross-linked polymers.

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Sulfoethylation of polymers represents a productive procedure for polymer-analogous transformations, since incorporation of a strong acid residue into the macromolecule substantially modifies the properties of the initial polymer. For example, 2-sulfoetylation of synthetic polymers allows preparation of stationary phases for HPLC [1, 2], ion-conducting membranes [3], catalysts [4, 5], and antimicrobial agents [6]. In the case of natural polymers, modification with 2-sulfoethyl groups has gained wider acceptance as a method of preparation of products suitable for manufacture of membranes intended for various applications [7, 8], biopolymeric surfactants [9, 10], and 3d-metal ion sorbents [11, 12]. Modification significantly affects the bioactive properties of the initial polymer matrices; the modified polymers exhibit antimutagenic [13–16], immunomodulating [17], and anticoagulant [18] activity.

Chitosan is a linear amino polysaccharide whose structure is nearly identical to that of cellulose, except for the fact that the pyranose ring bears an amino, instead of a hydroxy, group on the C-2 position, whereby it acquires high complexing power with respect to metal ions. The presence of highly reactive amino and hydroxy groups in chitosan allows for easy modification and extends the application range of the polymer.

Sulfoethylation of chitosan and carboxymethylated chitosan with sodium 2-chloroethanesulfonate [18, 19] and sodium vinyl sulfonate [12] in a strongly alkaline medium leads to nonselective N,O-substituted product.

Here, we developed a procedure for synthesis of N-2-sulfoethyl chitosan (SEC), a promising derivative of the amino-containing polymer of natural origin, and examined its sorption properties with respect to transition and alkaline-earth metal ions.

EXPERIMENTAL

We used chitosan available from Sonat (degree of deacetylation 0.84, molecular weight 250 kDa, ash residue 0.19%). The degree of deacetylation was determined by ^{1}H NMR spectroscopy, and the molecular weight, viscometrically [20]; sodium 2-bromoethanesulfonate was available from Alfa Aesar and used without further purification.

For C,H,N analysis served a Perkin Elmer automatic analyzer. The diffuse reflection IR spectra were measured

on a Perkin Elmer Spectrum-One spectrometer. The ^{1}H NMR spectra were recorded on a Bruker DRX-400 spectrometer, with sodium 3-(trimethylsilyl)-1-propanesulfonate (DSS) as internal reference. The samples were dissolved in D_2O/DCl (10 mg ml^{-1}); the solvent signal was suppressed by presaturation.

In a typical procedure of polymer-analogous transformations, a mixture of 3.3 g (0.02 mol) of chitosan, 13 ml of water, and 0.9 ml (0.01 mol) of 34% hydrochloric acid were kept for 10 min until a gel-like mass was formed, after which 20 g (0.04 mol) of sodium 2-bromoethanesulfonate was added. The resulting mixture was thoroughly stirred, heated to 70°C for 24 h, and cooled, after which 0.8 g (0.01 mol) of NaOH dissolved in 50 ml of water was added. After homogenization, 300 ml of acetone was added to the solution, resulting in precipitation of the product which was subsequently extracted with hot ethanol for 24 h. The resulting product was dried at 50°C to constant weight. Yield 4.5 g. The conditions of modification and characteristics of the products are summarized in the table. The ^{1}H NMR spectrum of N-2-sulfoethyl chitosan (D_2O/DCl), δ, ppm: 2.08 (C<u>H</u>$_3$), 3.23 (H-2 GlcN<u>H</u>$_2$), 3.35 (NHC<u>H</u>$_2$CH$_2$), 3.44–4.10 (H-2,3,4,5,6, NHCH$_2$C<u>H</u>$_2$), 4.62 (H-1 GlcNHAc), 4.94 (H-1 GlcNH$_2$), 5.04 (H-1 GlcNHCH$_2$CH$_2$).

Conditions of 2-sulfoethylation of chitosan with sodium 2-bromoethanesulfonate and characteristics of the resulting products, 24 h

Reaction conditions			*S*, %	DS[a]
chitosan : reagent : HCl molar ratio	gel concentration, %	*T*, °C		
Increase in HCl amount				
1 : 1 : 0.25	21	70	5.06	0.31
1 : 1 : 0.5	23	70	4.17	0.24
1 : 1 : 1	20	70	0.20	0
Changes in temperature and concentration				
		50	5.24	0.30
1 : 2 : 0.25	23	70	6.55	0.44
		90	6.23	0.46
1 : 2 : 0.5	23	50	3.44	0.16
	10	70	4.64	0.24
	20	70	7.12	0.50
	30	70	4.12	0.24
1 : 2 : 0.5[b]	20	70	6.45	0.40
Increase in reagent amount				
1 : 3 : 0.25	23	50	6.87	0.33
1 : 3 : 0.5	23	50	3.28	0.16
		70	4.86	0.30

[a] The degree of substitution was calculated using the ^{1}H NMR spectroscopic data.

[b] Acetic acid was used instead of hydrochloric acid.

The degree of substitution of the products was calculated with the use of the ^{1}H NMR spectroscopic data by the formula DS = (m)/(m+a), where m is the mole fraction of silfoethylated glucosamine units, and a, mole fraction of glucosamine units. The parameters m and a were estimated from the integral intensities of the corresponding ^{1}H NMR signals.

For preparation of sorbents, the polymers were preliminarily cross-linked, to which end 3.75 g of SEC was dissolved in 35 ml of water, and this was followed by adding a 34% HCl solution under stirring to pH 3.

Glutaric aldehyde (25% solution, 12 ml) was added to the resulting solution under stirring, and the mixture was kept at 60°C for 24 h. The resulting gel was ground, rinsed with water until pH of the washing water and lacking Cl^- ions in filtrate, and dried at 50°C to constant weight.

Next, we studied the selectivity of sorption of copper(II), silver(I), nickel(II), cobalt(II), zinc(II), cadmium(II), lead(II), manganese(II), calcium(II), magnesium(II), strontium(II), and barium(II) ions by cross-linked N-2-sulfoethyl chitosan from solutions containing each of the ions in the concentration of $n \times 10^{-4}$ M in the pH range 2.0–10.0 (ammonium acetate buffer). The experiments were performed under static conditions, using the limited volume method, with regular stirring for 7 days.

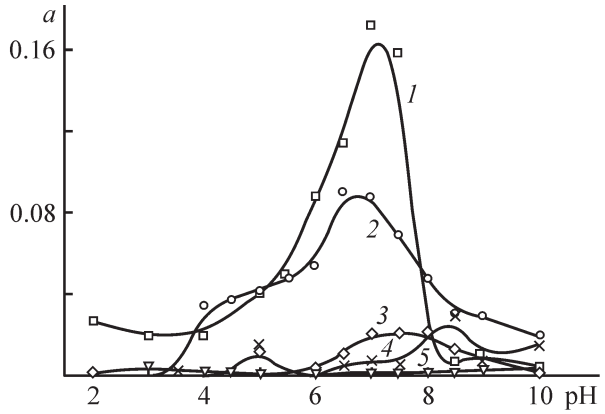
The concentration of the metal ions in the solutions before and after sorption was determined by inductively-coupled plasma atomic emission spectroscopy on a Thermo Scientific iCAP 6500 spectrometer. The amount of the metal ion sorbed was estimated from the difference in the concentrations of the analyzed ion in solution above the sorbent before and after sorption. An I-160MI ion meter supplied with an ESK-10601/7 combined glass electrode served for monitoring of pH of the solutions.

The above-described procedure of preparation of N,O-2-sulfoethyl chitosan by the nucleophilic substitution reaction of chitosan with sodium 2-chloroethanesulfonate is carried out under heterogeneous conditions of modification [12, 18], since the solvent used is isopropanol or its mixture with xylene. This modification procedure

can give a product with the degree of substitution of no greater than 0.35. To prepare a chitosan derivative with a higher degree of substitution, we employed the "synthesis in a gel" procedure for polymer-analogous transformations, which was successfully applied by us previously in chitosan carboxyalkylation reactions [21, 22] (see the scheme).

The composition and structure of the resulting polymers were confirmed by elemental analysis and IR spectroscopy. Against background of intense absorption bands characteristic of chitosan, N–H, O–H (3376 cm^{-1}), C–H (2881 cm^{-1}), C=O amide I (1652 cm^{-1}), residual acetyl groups, C–O and C–C (1067 cm^{-1}), the spectra contained new very intense bands corresponding to vibrations of the sulfonate group, S=O (1164, 1040 cm^{-1}). The nature of regioselectivity of the substitution reaction was identified using ^1H NMR spectroscopy. The spectrum of the 2-sulfoethylated product contains a signal at 5.06 ppm corresponding to H-1 atom of the glucopyranose ring bearing a secondary amino group. Thus, like with chitosan carboxyalkylation [22–24], 2-sulfoethylation under nonalkaline conditions leads to selectively N-substituted polymer.

The table summarizes the conditions of the polymer-analogous transformations and the corresponding DS values. The reaction mixture is a gel which is kept at a certain temperature without stirring. The use of chitosan in its chlorohydrate form is necessary for formation of a physical gel, but a hydrochloric acid excess leads to reduction in DS. A change from hydrochloric to acetic acid in gel formation has virtually no effect on DS. A more than twofold increase in the molar excess of sodium 2-bromoethanesulfonate over amino groups seems unreasonable,

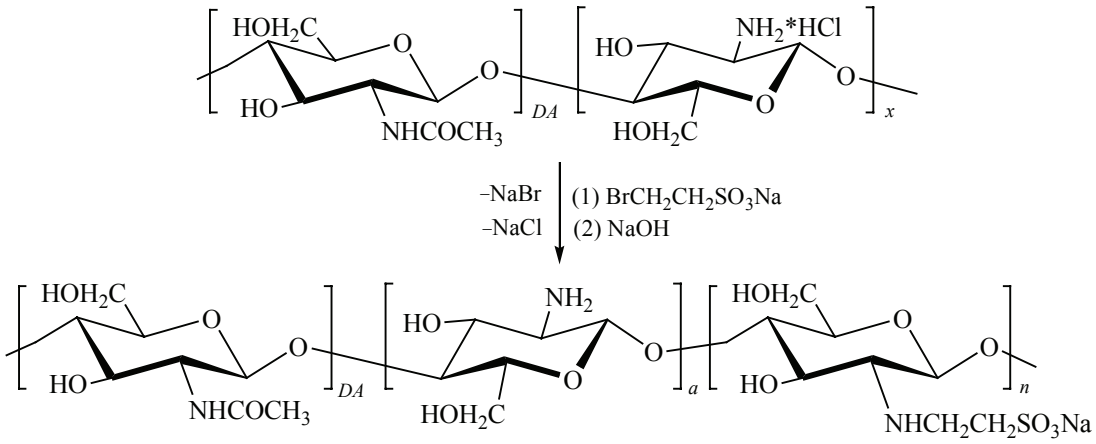


The pH dependence of sorption a, mmol g^{-1}, of the metal ions by SEC with DS 0.3. Ammonium acetate buffer solution; initial concentration of the metal ions 10^{-4} M. (*1*) Ag(I), (*2*) Cu(II), (*3*) Ni(II), (*4*) Co(II), and (*5*) Ba(II).

as it does not lead to a substantial increase in the degree of substitution. Like in the case of alkylation of chitosan by 3-halopropionic acids [22], a gel-effect of polymer-analogous transformation is observed as manifested in the existence of an optimal gel concentration which affords the maximal derivatization. In the case of interest, this concentration is 20%. The optimal reaction temperature is 70°C: At a lower temperature, DS is half as large, while an increase in the reaction temperature to 90°C causes only slight increase in the degree of substitution.

In this study, chelate sorbents based on SEC were prepared by cross-linking of the polymer with glutaric aldehyde. To evaluate the promise of these sorbents for separation and concentration of metal ions, we studied the sorption selectivity for silver(I), copper(II), zinc(II), nickel(II), cobalt(II), cadmium(II), lead(II),

Scheme.



manganese(II), calcium(II), strontium(II), magnesium(II), and barium(II) coexisting in an ammonium acetate buffer solution. The figure presents the pH dependences of sorption for Ag(I), Cu(II), Ba(II), Ni(II), and Co(II) ions. For the remaining metal ions, the sorption capacity does not exceed 0.02 mmol g^{-1}. It is seen that the sorbent based on SEC with DS of 0.3 selectively recovers silver(I) and copper(II) ions. The optimal pH range for the recovery of these metal ions from ammonium acetate buffer solution is 6.0–7.5. It should be noted that barium(II) ions are not sorbed at all. Therefore, in the case of silver(I) ions, the sorption selectivity is associated with formation of a coordination compound rather than of an insoluble salt. Thus, the SEC-based sorbents are promising materials for concentration of silver(I) and copper(II) ions from multicomponent ammonium acetate solutions.

CONCLUSIONS

(1) A new procedure was proposed for polymer-analogous transformation of chitosan through the 2-sulfoethylation reaction, leading to selectively N-substituted product with the average degree of substitution of up to 0.5.

(2) Cross-linked N-2-sulfoethyl chitosans are suitable as sorbents for selective separation of silver(I) and copper(II) ions from several interfering transition and alkaline-earth metal ions.

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